FLUID LOSS CONTROL AND SEALING AGENT
FOR DRILLING DEPLETED SAND FORMATIONS

Cross-Reference to Related Application

5   **[0001]**   This application is a continuation-in-part of U.S. Patent Application Serial No. 09/785,842 filed on February 16, 2001, now pending.

Field of the Invention

[0002]   The present invention relates to oil-based drilling fluids used during 10   petroleum recovery operations, and more particularly relates, in one embodiment, to using oil-based drilling fluids containing additives to inhibit fluid loss in the drilling of depleted sand formations.

Background of the Invention

15   **[0003]**   Drilling fluids used in the drilling of subterranean oil and gas wells as well as other drilling fluid applications and drilling procedures are known. In rotary drilling there are a variety of functions and characteristics that are expected of drilling fluids, also known as drilling muds, or simply "muds". The drilling fluid is expected to carry cuttings up from beneath the bit, transport them up the annulus, 20   and allow their separation at the surface while at the same time the rotary bit is cooled and cleaned. A drilling mud is also intended to reduce friction between the drill string and the sides of the hole while maintaining the stability of uncased sections of the borehole. The drilling fluid is formulated to prevent unwanted influxes of formation fluids from permeable rocks penetrated and also often to form 25   a thin, low permeability filter cake which temporarily seals pores, other openings and formations penetrated by the bit. The drilling fluid may also be used to collect and interpret information available from drill cuttings, cores and electrical logs. It will be appreciated that within the scope of the claimed invention herein, the term "drilling fluid" also encompasses "drill-in fluids".

30   **[0004]**   Drilling fluids are typically classified according to their base material. In water-based muds, solid particles are suspended in water or brine. Oil can be

emulsified in the water or brine. Nonetheless, the water is the continuous phase. Oil-based muds are the opposite. Solid particles are suspended in oil and water or brine is emulsified in the oil and therefore the oil is the continuous phase. Oil-based muds that are water-in-oil emulsions are also called invert emulsions. Brine-based

5   drilling fluids, of course are a water-based mud in which the aqueous component is brine.

[0005]   Optimizing high performance water base mud design is commonly at the forefront of many drilling fluid service and oil operating companies' needs due to the various limitations of invert emulsion fluids. Invert emulsion fluids formulated

10   with traditional diesel, mineral or the newer synthetic oils are the highest performing drilling fluids with regard to shale inhibition, borehole stability, and lubricity. Various limitations of these fluids, however, such as environmental concerns, economics, lost circulation tendencies, kick detection, and geologic evaluation concerns maintains a strong market for high performance water based fluids. Increased

15   environmental concerns and liabilities continue to create an industry need for water based drilling fluids to supplement or replace the performance leading invert emulsion mud performance.

[0006]   A particular problem when drilling into shale formations with water-based fluids is the pore pressure increase and swelling from penetration of the

20   shale by the fluid. Shale stabilizers are typically added to the mud to inhibit these phenomena and to stabilize the shale from being affected by the mud.

[0007]   Reducing drilling fluid pressure invasion into the wall of a borehole is one of the most important factors in maintaining wellbore stability. It is recognized that sufficient borehole pressure will stabilize shales to maintain the integrity of the

25   borehole. When mud or liquid invades the shale, the pressure in the pores rises and the pressure differential between the mud column and the shale falls. With the drop in differential pressure, the shale is no longer supported and can easily break off and fall into the well bore. Likewise, the invasion of water into the shale matrix increases hydration or wetting of the partially dehydrated shale body causing it to

30   soften and to lose its structural strength. Chemical reactivity can also lead to

instability. There is always a need for a better composition and method to stabilize the shale formations.

[0008] There is an analogous need to seal and prevent fluid loss control when recovering hydrocarbons from sand formations, particularly depleted sand

5 formations. Depleted sand formations are productive, or formerly productive, hydrocarbon zones that have been produced, drawn down, or otherwise depleted of their content, creating a lower formation pressure than that of the fluid which may be in use in the well. Because of this pressure differential, it is important to partially or completely seal the sand formation to inhibit or prevent fluid loss of the mud into

10 the sand.

[0009] It is apparent to those selecting or using a drilling fluid for oil and/or gas exploration that an essential component of a selected fluid is that it be properly balanced to achieve all of the necessary characteristics for the specific end application. Because the drilling fluids are called upon to do a number of tasks

15 simultaneously, this desirable balance is difficult to achieve.

[0010] It would be desirable if compositions and methods could be devised to aid and improve the ability of drilling fluids to simultaneously accomplish these tasks.

20   Summary of the Invention

[0011] Accordingly, it is an object of the present invention to provide methods and compositions to at least partially seal subterranean sand formations when conducting hydrocarbon recovery operations with oil-based drilling fluids.

[0012] It is another object of the present invention to provide oil-based

25 drilling fluids that reduce the rate of drilling fluid pressure invasion into the borehole wall.

[0013] Still another object of the invention is to provide a composition and method that increase the pressure blockage and reliability of sand formation seals that can be accomplished with oil-based fluids.

[0014]   In carrying out these and other objects of the invention, there is provided, in one form, an oil-based drilling fluid for use in sealing sand formations that includes a polymer latex that is capable of providing a deformable latex film on at least a portion of a subterranean formation. The latex includes polymer particles

5   in an aqueous continuous phase. The oil based drilling fluid additionally includes a hydrocarbon base fluid and an emulsifier.

[0015]   In another non-limiting embodiment of the invention, there is provided, in one form, a method of inhibiting fluid loss of an oil-based drilling fluid in a sand formation, where the method involves providing an oil-based drilling fluid. The oil-

10   based drilling fluid includes a polymer latex capable of providing a deformable latex film on at least a portion of a subterranean formation. In turn, the latex includes polymer particles in an aqueous continuous phase. The oil-based drilling fluid also includes a hydrocarbon base fluid and an emulsifier. The method additionally comprises circulating the oil-based drilling fluid in contact with a borehole wall.

15

Brief Description of the Drawings

[0016]   FIG. 1 shows a chart of the formation pressure as a function of time for a pressure invasion test using various intermediate test formulations;

[0017]   FIG. 2 is a graph of the surfactant effect on GENCAL 7463 particle

20   size in 20% NaCl/1 lb/bbl NEWDRILL PLUS/ 1 lb/bbl XAN-PLEX D/0.5 lb/bbl sodium gluconate/3 lb/bbl NaAlO2/5% by volume GENCAL 7463;

[0018]   FIG. 3 is a graph of the influence of polymer resins (3 lb/bbl) on GENCAL 7463 particle size distributions after 16 hours, 150°F hot roll in 20% NaCl/0.75 lb/bbl XAN-PLEX D/0.5 lb/bbl sodium D-gluconate/0.4 lb/bbl NEW-DRILL

25   PLUS/2 lb/bbl BIO-PAQ/3 lb/bbl NaAlO2/3% GENCAL 7463/1 lb/bbl EXP-152;

[0019]   FIG. 4 is a graphical comparison of the effects on mud properties for EXP-154 versus ALPLEX in 12 lb/gal mud; the base mud was 20% NaCl/0.5 lb/bbl XAN-PLEX D/2 lb/bbl BIO-LOSE/1 lb/bbl NEW-DRILL PLUS/3% EXP-155/150 lb/bbl MIL-BAR/27 lb/bbl Rev Dust;

[0020]   FIG. 5 is a graph of PPT test results for ALPLEX, EXP-154/EXP-155, and ISO-TEQ fluids;

[0021]   FIG. 6 is a graph showing the effect of circulation on EXP-154/EXP-155 mud performance;

5   **[0022]**   FIG. 7 is a graph showing the effect of latex on mud properties in 9.6 lb/gal 20% NaCl fluid after 16 hours, 250°F (121°C) hot roll; the base fluid was 20% NaCl/1 lb/bbl XAN-PLEX D/0.4 lb/bbl NEW-DRILL PLUS/2 lb/bbl BIO-PAQ/5 lb/bbl EXP-154/10 lb/bbl MIL-CARB/27 lb/bbl Rev Dust;

[0023]   FIG. 8 is a graph showing the effect of latex on mud properties in 12

10   lb/gal after hot rolling for 16 hours at 250°F (121°C); the base fluid was 20% NaCl/0.75 lb/bbl XAN-PLEX D/0.4 lb/bbl NEW-DRILL PLUS/3 lb/bbl BIO-PAQ/5 lb/bbl EXP-154/150 lb/bbl MIL-CARB/27 lb/bbl Rev Dust; and

[0024]   FIG. 9 is a graph of 96 hour Mysidopsis bahia range-finder results for experimental products in 12 lb/gal fluids where the base fluid is 20% NaCl/0.5 lb/bbl

15   XAN-PLEX D/0.4-1 lb/bbl NEW-DRILL PLUS/2 lb/bbl MIL-PAC LV (or BIO-PAQ)/150 lb/bbl MIL-BAR;

[0025]   FIG. 10 is a graph of polymer particle size distribution of MAX-SEAL in a polyolefin hydrocarbon base fluid;

[0026]   FIG. 11 is a chart of the effect of MAX-SEAL on PPA test results at

20   250° F (121°C) for 14 lb/gal SYN-TEQ mud on different permeability disks, where the mud samples have been hot rolled at 250°F (121°C) for 16 hours; and

[0027]   FIG. 12 is a graph of the effect of MAX-SEAL on the PPA fluid loss at 250° F (121°C) on 0.4 Darcy disk for 14 ppg SYN-TEQ mud, where the mud samples have been hot rolled at 250°F (121°C) for 16 hours.

25

Detailed Description of the Invention

[0028]   It has been discovered that a polymer latex added to a water-based drilling fluid can reduce the rate the drilling fluid pressure invades the borehole wall of a subterranean formation during drilling. The polymer latex preferably is capable

30   of providing a deformable latex film or seal on at least a portion of a subterranean

formation. Within the context of this invention, the terms "film" or "seal" are not intended to mean a completely impermeable layer. The seal is considered to be semi-permeable, but nevertheless at least partially blocking of fluid transmission sufficient to result in a great improvement in osmotic efficiency. In a specific, non-

5 limiting embodiment, a submicron polymer latex added to a high salt water-based mud containing an optional, but preferred combining/precipitating agent, such as an aluminum complex will substantially reduce the rate of mud pressure penetration into shale formations. The pressure blockage, reliability, magnitude and pore size that can be blocked are all increased by the latex addition. Inhibiting drilling fluid

10 pressure invasion into the wall of a borehole is one of the most important factors in maintaining wellbore stability.

[0029]   It has been additionally discovered that the polymer latex systems of this invention can be incorporated into oil-based drilling fluids. However, it has been discovered that in these fluids, the polymer latex seals can be formed without the

15 need for a precipitating agent, a surfactant or any salt in the water phase. The latex, where generally water or other aqueous component is the continuous phase, is in turn suspended in a hydrocarbon base fluid having at least an amount of emulsifier sufficient to suspend the polymer latex therein. In one non-limiting embodiment of the invention, the polymer latex may simply be mixed with the

20 hydrocarbon base fluid without the need for adding any more emulsifier than is normally present in such fluids.

[0030]   The components of the water-based drilling fluids of this invention are the polymer latex and water, which makes up the bulk of the fluid. Of course, a number of other common drilling fluid additives may be employed as well to help

25 balance the properties and tasks of the fluid.

[0031]   The polymer latex is preferably a carboxylated styrene/butadiene copolymer, in a non-limiting example. A particular, non-limiting carboxylated styrene/butadiene copolymer is GENCAL 7463 available from Omnova Solution Inc. Other suitable polymer latexes include, but are not limited to polymethyl

30 methacrylate, polyethylene, polyvinylacetate copolymer, polyvinyl acetate/vinyl chloride/ethylene copolymer, polyvinyl acetate/ethylene copolymer, natural latex,

polyisoprene, polydimethylsiloxane, and mixtures thereof. A somewhat less preferred polymer latex is polyvinylacetate copolymer latex, more specifically, an ethylenevinyl chloride vinylacetate copolymer. While polyvinylacetate copolymer latices will perform within the methods of this invention, they generally do not

5   perform as well as the carboxylated styrene/butadiene copolymers. The average particle size of the polymer latex is less than 1 micron or submicron in one non-limiting embodiment of the invention, and in another non-limiting embodiment has a diameter of about 0.2 microns or 0.2 microns or less. Other polymers in the disperse phase may be found to work. It is anticipated that more than one type of

10   polymer latex may be used simultaneously. The proportion of the polymer latex in the drilling mud, based on the total amount of the fluid may range from about 0.1 to about 10 vol.%, preferably from about 1 to about 8 vol.%, and most preferably from about 2 to about 5 vol.%. These ranges apply for the embodiment of oil-based drilling fluids as well.

15   **[0032]**   The optional salt may be any common salt used in brine-based (aqueous) drilling fluids, including, but not necessarily limited to calcium chloride, sodium chloride, potassium chloride, magnesium chloride, calcium bromide, sodium bromide, potassium bromide, calcium nitrate, sodium formate, potassium formate, cesium formate and mixtures thereof. By a "high salt content" is meant at least 20

20   weight percent, and saturated brine solutions are preferred in one non-limiting embodiment. It will appreciated that it is impossible to predict in advance what the salt content of a particular saturated brine solution will be since the saturation point depends on a number of factors including, but not limited to the kinds and proportions of the various components of the water-based fluid. The salt is optional

25   because the invention will perform without it, that is, using fresh water.

[0033]   Another optional component is precipitating agent. Suitable precipitating agents include, but are not limited to, silicates, aluminum complexes, and mixtures thereof. Suitable aluminum complexes include, but are not limited to, sodium aluminate, NaAl2O2, sometimes written as Na2OAl2O3, aluminum

30   hydroxide, aluminum sulfate, aluminum acetate, aluminum nitrate, potassium aluminate, and the like, and mixtures thereof (especially at pH of >9 for these

compounds to be soluble in water). The proportion of the precipitating agent in the drilling mud, based on the total amount of the fluid may range from about 0.25 to about 20 lb/bbl, preferably from about 1 to about 10 lb/bbl and most preferably from about 2 to about 7 lb/bbl. Without being limited to a particular theory, the

5 precipitating agent is believed to chemically bind to the surface of the clay of the borehole and provide a highly active polar surface.

[0034] Another optional component of the composition of the invention is a surfactant. If the surfactant is present, the surfactant treated latex wets the surface strongly and accumulates to form a film or coating that seals fractures and defects

10 in the shale. Suitable wetting surfactants include, but are not limited to, betaines, alkali metal alkylene acetates, sultaines, ether carboxylates, and mixtures thereof. It has been determined that surfactants are particularly beneficial when salts are present in the drilling fluid, and are not as preferred in fresh water fluid systems.

[0035] The proportions of these components based on the total water-based

15 drilling fluid are from about 0.1 to 10 volume% of polymer latex, at least 1 wt % of salt (if present), from about 0.25 to 20 lb/bbl of precipitating agent (if present), from about 0.005 to about 2 vol.% of surfactant (if present), the balance being water. In a more preferred embodiment, the proportions range from about 1 to 8 vol.% of polymer latex, at least 1 wt % of salt (if present), from about 1 to 10 lb/bbl of

20 precipitating agent (if present) from about 0.01 to about 1.75 vol. % of wetting surfactant (if present), the balance being water.

[0036] It is desired that the sodium aluminate or other precipitating agent be in a metastable form in the mud, which means that it is in suspension or solution, but precipitates out upon the borehole wall. Typically, aluminum compounds have

25 been added to the mud on site. If added to mud formulations earlier, they tend to be unstable and precipitate prematurely.

[0037] Since the development of pore pressure transmission (PPT) testing, the effects of various chemical additives on pore pressure transmission rates have been evaluated. Testing has focused primarily on the performance of salts, glycols,

30 and precipitating agents such as silicates and aluminum complexes. Improvements in PPT test equipment and methods have accompanied the general interest and

search for increasing more efficient water-based mud systems that approach the PPT test performance of invert emulsion fluids. While other investigators have found silicate fluids to be especially effective for reduced poor pressure transmission rates, silicate fluids have not been widely used due to limitations of

5 these fluids. Although lower pore pressure transmission rates have been demonstrated for salts, glycols, and aluminum complexing agents, these products still do not approach the performance of invert emulsion fluids.

[0038] A combination of a new formulation approach as well as modification to the PPT test procedure was used to demonstrate the efficacy of an alternative

10 approach to enhance the performance of water-based mud systems. Water-dispersible polymers were selected to provide sources of small, deformable particles to provide a sealing and blocking effect on the shale. The first of these polymers was tested on the PPT test in a fluid with other products.

[0039] In another embodiment of the invention, the polymer latex is

15 suspended in a hydrocarbon base fluid, also known as an oil-based fluid. The hydrocarbon phase may be any suitable hydrocarbon used in drilling fluid applications including, but not necessarily limited to diesel, synthetic hydrocarbons, such as isomerized polyolefins and the like. Hydrocarbon base fluids used as drilling muds typically contain emulsifiers that are necessary to achieve the multiple

20 functions of the mud. These emulsifiers are all suitable to suspend the latex in the hydrocarbon base fluid. The latex itself is suspended as "particles" in the hydrocarbon base fluid phase. The size of these particles is typically larger than the size of the polymer particles in the latex and may range up to 100 microns in one non-limiting embodiment of the invention, and from about 10 to about 100 or less

25 than 100 microns in an alternate embodiment. In another non-limiting, alternate embodiment, the polymer particles *per se* may range from about 1 to 100 microns in one non-limiting embodiment, and may range between about 0.3 and 10 microns or less, in another non-limiting embodiment may range from about 0.8 to less than 10 microns, where in another non-limiting embodiment, the particles have an

30 average particle size between about 1 and 10 microns, and more preferably from about 1 to about 7 microns.

[0040] The invention will be further illustrated with respect to the following examples, which are only meant to further illuminate the invention, and not limit it in any way.

EXAMPLE 1

Fluid Intermediate Preparation

[0041] The following Example is the first preparation of the intermediate compositions of this invention. Unless otherwise noted, the latex in the Examples is 728 Latex, a polyvinylacetate latex.

Component	Grams per barrel	Grams per 7 barrels
Tap water	310	2170
Sodium aluminate	2	14
LIGCO	2	14
AIRFLEX 728	10.5	73.5 (75 cc)

The mixture was hot rolled. After 6 days, the pH was 11.51. The bottom of the jar was about 75% covered with $^1/_{32}$" fines. The following components were then added, again given in gram proportions for a single barrel and 7 barrels, respectively:

NEWDRILL PLUS	0.4	2.8
NaCl (20%)	77.5	540
MILPAC LV	2	14

The fluid with the latex and the NEWDRILL+ had a light brown color. LD8 was added to control foaming. The resulting mixture was hot rolled for four hours at 150°F. The final pH was 10.75.

EXAMPLE 2

Shale Pressure Penetration Determination

[0042] The pore pressure transmission (PPT) device is based on a 1500 psi Hassler cell designed for 2.5cm diameter core plugs from 2.5cm to 7.5cm in length.

A Hassler cell is a cylinder with a piston inserted in each end. The core is held between the two pistons. A rubber sleeve is placed around the core and the pistons to seal around the core and prevent flow around the core. The outside of the sleeve is pressured to make a good seal. These tests use a core 25 mm in diameter and 25mm long.

[0043] The low pressure side of the core (formation side) is fitted with a 1 liter, 2000 psi., stainless steel accumulator to provide back pressure. The high pressure side of the core is connected to two similar accumulators, one for pore fluid, and one for the test fluid. The pressure in each accumulator is controlled with a manual regulator fed by a 2200 psi nitrogen bottle.

[0044] All pressures are monitored with Heise transducers. The transducer pressures are automatically computer logged at preset intervals.

[0045] The cell is enclosed in an insulated chamber and the temperature maintained with a 200 watt heater. The heater is controlled with a Dwyer temperature controller driving a Control Concepts phase angle SCR control unit. Temperature control is accurate to +/- 0.05 °C.

[0046] A pressure is applied to one end of the core and the flow through the core is measured. The piston on the low pressure side is filled with liquid, and blocked, so an increase in liquid pressure is measured rather than flow. A very small amount of liquid flow through the core will make a large rise in the pressure, making the cell sensitive enough to measure flow through shale. Shale has a very low permeability, so the flow of fluid through it is very small. Pressure is plotted versus time. Results are expressed as formation pressure (FP). If the FP increases over time, there is pressure penetration; if the formation pressure decreases over time there is not, and the latter is what is desired.

[0047]   The fluid of Example 1 was used. Three 50% displacements of 50 cc each were performed during and just after heating up of the test cell. One run was started at 100% displacement and the temperature was difficult to control, so it was decided starting at 50% was better.

5

Temperature = 155°F

Borehole side pressure = 250 psi

Confining pressure = 370 psi

Time, hours:minutes	Formation Pressure, psi
0	48.1
1:30	47.9
2:00	47.6
7:15	50.9

10   Eventually, 50 cc of fluid was displaced up to 50% within 2°F temperature variation. The pressure rose to 52.7 psi. Formation heat was turned off, and the temperature was 147°F. Displacement pulled the formation pressure down to 36 psi, then rose to 80.2 over the next two days. The initial formation pressure decrease demonstrated that the formulation of the invention inhibited pressure penetration.

15

EXAMPLE 3

Fluid Intermediate Preparation – proportions in grams unless otherwise noted

Component	Per barrel	Per 7 barrels
Tap water	310	2170 cc
Sodium aluminate	2	14
LIGCO	2	14
AIRFLEX 728 Latex	10.5	75 cc
NEWDRILL PLUS	0.4	2.8
NaCl (20%)	77.5	540
MILPAC LV	2	14

The sodium aluminate and AIRFLEX 728 latex were mixed together and allowed to stand over the weekend. The mixture was then hot rolled at 150°F for two hours. The salt and polymers were then added. The sequence of addition to the sodium aluminate/latex mixture was: PHPA (partially hydrolyzed polyacrylamide; NEWDRILL PLUS), followed by mixing; then half of the salt, followed by MILPAC LV, followed by the other half of the salt. The mixture was hot rolled overnight.

5

EXAMPLE 4

10

Shale Pressure Penetration Determination

Borehole side pressure = 250 psi

Confining pressure = 370 psi

Time, hours:minutes	Formation Pressure, psi
0	46.3
5:49	2.3
7:36	0.6*
50:00	65.0

* The confining pressure was raised to 410 psi and the borehole pressure was

15 raised to 300 psi at this point.

EXAMPLES 5 and 6, COMPARATIVE EXAMPLES A-F

[0048]   Two other inventive formulations (Examples 5 and 6) and six comparative Examples (A-F) were prepared and tested. The results are shown in

20 FIG. 1. As indicated the Inventive Examples 5 and 6 both gave the desired results of decreasing formation pressure over time. The comparative Examples undesirably gave increasing formation pressures over time. The composition identities are given on FIG. 1 itself. The designation "CORE: P2 PARALLEL" refers to the core being Pierre Shale in parallel orientation.

[0049] These results verify the necessity of having all three components: the salt, the latex, and the sodium aluminate (Examples 5 and 6). Use of the latex alone (comparative Ex. A), use of salt only (comparative Ex. B), use of the latex together with salt only (comparative Example C), use of sodium aluminate and the
5   salt only (comparative Ex. D), use of the sodium aluminate and salt only (comparative Ex. E), and use of the sodium aluminate with salt only (comparative Ex. F) were all found to be ineffective, or at least certainly not as effective as the inventive composition.

[0050] Further experimental evidence indicates that some latex products
10   exhibit a synergistic effect with aluminum complexes that results in improved pore pressure transmission characteristics. Stable drilling fluid systems have been formulated with latex that remain dispersed and flexible in highly saline (high salt content) fluids. Inventive drilling fluids provide pore pressure transmission performance closer to oil-based fluids than what is exhibited by current aluminum-
15   based drilling fluids. Two features of this system are believed to be the main contributors to shale stabilization. First, the ultra-fine, deformable latex particles (having a preferable diameter of about 0.2 microns) mechanically seal shale micro-fractures and physically prevent further intrusion of drilling fluids into sensitive shale zones. Secondly, latex co-precipitation with precipitating agents, if present, such as
20   aluminum complexes, produces a semi-permeable membrane on shale surfaces that chemically improves the osmotic efficiency between the fluid and the borehole.

[0051] Three experimental additives were discovered for the inventive fluids: EXP-153, EXP-154 and EXP-155. EXP-153 is a sulfonated polymer resin used to control HTHP fluid loss in this system. EXP-154 is considered an alternative to
25   aluminum complex product ALPLEX. Compared to ALPLEX, EXP-154 exhibits much better compatibility with latex fluids. EXP-155 is a modified latex product. Compared to other commercially available latices EXP-155 displays less sensitivity to electrolytes and does not flocculate in 20% sodium chloride fluids at temperatures up to 300°F (149°C). Furthermore, due to the wide temperature range
30   between its glass transition temperature (Tg) and melting point (Tm), the particles

of EXP-155 remain deformable and capable of plugging shale micro-fractures at most application temperatures. The toxicities of all of these products meet the requirement for fluid disposal in the Gulf of Mexico.

5   Formulations and Fluid Properties

[0052]   All fluids were mixed according to established Baker Hughes INTEQ mixing procedures. The initial and final Bingham Plastic rheological properties of plastic viscosity, yield point, ten second gels, and ten minute gels were measured by Fann 35 viscometer at 120°F (49°C). The initial and final pH and API filtrate

10   were recorded. HTHP fluid loss at 250°F (121°C) was measured after static and dynamic aging for 16 hours at 250°F (121°C).

Latex Stability

The stability of the latex samples were first evaluated in 20% and 26% NaCl

15   solutions by the following procedure:

1.   Add 332 ml 20% (or 26%) NaCl water solution into a mixer cup and start mixing.

2.   Slowly add 18 ml tested latex sample into the solution and adjust the Prince Castle mixer to 4000 rpm with Variac and tachometer.

20   3.   After stirring 5 minutes, slowly add 3 grams $NaAlO_2$ into the above solution and mix for a total of 20 minutes. During the mixing period it may be necessary to add about 5 drops defoamer (LD-8) if foaming is observed.

4.   Put this fluid into a jar and statically age for 16 hours at 150°F (66°C).

5.   Remove the jar from the oven and cool to room temperature. Observe the

25   fluid for flocculation and separation.

6.   If there is no separation or flocculation, sieve the fluid with a 100-mesh (0.150 mm) [please check this conversion, if possible] screen. Observe sieve for amount of retained latex particles.

[0053]   Additional evaluations were performed only for those samples having passed the above screening test. A Malvern Mastersizer Particle Size Analyzer was used to measure the particles size distributions of latex in formulated fluids. The small sample dispersion unit and the standard refractive index 50HD (Particle R.I. = 1.5295, 0.1000 and Dispersant R.I. = 1.3300) were used in all of the particle size distribution tests. 20% NaCl water solution with pH adjusted to 11.5.

Shale Inhibition Test

[0054]   The shale inhibition characteristics were determined by shale dispersion tests that included static wafer test, and pore pressure (PPT) tests. In the PPT test, a preserved Pierre II shale core, 1 inch diameter by 0.9 inch long (2.54 cm x 2.29 cm long), is placed between two pistons, as described previously in Example 2. The circumference of the shale and pistons are sealed with a rubber sleeve. The plug is oriented with the bedding planes in the parallel or high permeability direction. Drilling fluid at 300 psi is displaced through the upstream piston (borehole side) and seawater at 50 psi is displaced through the downstream piston (formation side). The seawater in the downstream piston is contained with a valve. As mud filtrate enters the borehole end of the plug, connate water in the shale is displaced into the formation piston.

Latex Stability

[0055]   As noted above, initial experiments indicated that some latex products (emulsion polymers) produced synergistic effects with an aluminum complex, resulting in improved pore pressure transmission characteristics of the fluids. This result revealed a new approach to the design of highly inhibitive, water-based fluids. However, latex is generally considered to be a metastable system. The large surface of the particles is thermodynamically unstable and any perturbation affecting the balancing forces stabilizing the polymer dispersion results in a change in the kinetics of particle agglomeration. Most commercial latices, which are designed for the production of synthetic rubber or the application of

painting/coating, are sensitive to increasing electrolytic concentration and temperature.

[0056] As shown in Table I, among 16 latex samples tested in 26% and 20% NaCl solutions, none of them is stable in 26% NaCl and only AIRFLEX 728 and

5   GENCAL 7463 are relatively stable in 20% NaCl. Clearly, for successful applications of latex in drilling fluids, latex stability in high salt environments and at elevated temperatures must be improved. A common technique used to increase latex stability in electrolyte solutions is the addition of some surfactants. FIG. 2 compares the effect of EXP-152 on the particle size distributions of AIRFLEX 728

10   with that of GENCAL 7463. These results indicate that a blend of GENCAL 7463 and EXP-152 may be a stable product for drilling fluid applications.

TABLE I

Stability Test for Latex Products in NaCl Solution

Ex.	Latex Samples	T_g (°C)	Stability After 16 Hours Static Aging	
			26% NaCl/3 lb/bbl NaAlO₂	20% NaCl/3 lb/bbl NaAlO₂

Vinyl Acetate/Ethylene Vinyl Chloride

Ex.	Latex Samples	T_g (°C)	26% NaCl/3 lb/bbl NaAlO₂	20% NaCl/3 lb/bbl NaAlO₂
7	AIRFLEX 728	0	Flocculation but pass 100 mesh	Flocculation/Coagulation

Vinyl Acetate/Ethylene

Ex.	Latex Samples	T_g (°C)	26% NaCl/3 lb/bbl NaAlO₂	20% NaCl/3 lb/bbl NaAlO₂
8	AIRFLEX 426	0	Flocculation/Coagulation	Flocculation/Coagulation
9	AIRFLEX 7200	0	Flocculation/Coagulation	Flocculation/Coagulation
10	VINAC XX-211	N/A	Flocculation/Coagulation	Flocculation/Coagulation
11	ELVACE 40722-00	N/A	Flocculation/Coagulation	Flocculation/Coagulation

Carboxylated Styrene/Butadiene

Ex.	Latex Samples	T_g (°C)	26% NaCl/3 lb/bbl NaAlO₂	20% NaCl/3 lb/bbl NaAlO₂
12	GENCAL 7463	13	Flocculation but pass 100 mesh	Floc. at 150°F (66°C) but stable at 75°F (24°C)
13	GENCAL 7470	N/A	Flocculation/Coagulation	--
14	GENFLO 576	N/A	Flocculation/Coagulation	--
15	TYLAC 68219	N/A	Flocculation but pass 100 mesh	Flocculation but pass 100 mesh
16	TYLAC CPS 812	N/A	Flocculation/Coagulation	--
17	TYCHEM 68710	N/A	Flocculation/Coagulation	--
18	ROVENE 9410	-56	Coagulation	Coagulation
19	ROVENE 6140	-27	Coagulation	Coagulation

Carboxylated Acrylic Copolymer

Ex.	Latex Samples	T_g (°C)	26% NaCl/3 lb/bbl NaAlO₂	20% NaCl/3 lb/bbl NaAlO₂
20	SYNTHEMUL CPS 401	N/A	Flocculation/Coagulation	--
21	SYNTHEMUL 97982	N/A	Flocculation/Coagulation	--

Styrene/Butadiene

Ex.	Latex Samples	T_g (°C)	26% NaCl/3 lb/bbl NaAlO₂	20% NaCl/3 lb/bbl NaAlO₂
22	ROVENE 4823L	-51	Coagulation	Coagulation

Aluminum Complex

[0057]   Although a synergistic effect of ALPLEX with latex on stabilizing shales was confirmed by PPT test results, this system is fragile and very sensitive to increasing salt concentration and temperature. It was found that in 20% NaCl

solution, 3% AIRFLEX 728 or 3% GENCAL 7463 were flocculated in a few minutes by adding 4 lb/bbl ALPLEX. Prehydration of ALPLEX in fresh water or addition of some surfactant (e.g. EXP-152) did improve the stability of this system at low temperatures, but the latex particle size was still greatly influenced by ALPLEX.

5 Those particles greater than 100 microns in the fluid containing ALPLEX may have partially resulted from insoluble lignite (a component of ALPLEX). A similar effect was also observed with GENCAL 7463. Poor solubility and slow dissolution rate of the lignite in high salt concentrations is probably the main factor contributing to decreased latex stability.

10 **[0058]** In order to find a polymer resin that was compatible with a latex system additional tests were performed. FIG. 3 shows the effects of different polymer resins on the particle size distributions of EXP-155. Among the tested samples, EXP-153 exhibited the best compatibility with this latex system.

[0059] A new aluminum complex product, EXP-154 (a blend of 45% NaAlO2, 15 45% EXP-153 and 10% sodium D-gluconate) was invented for the latex system. FIG. 4 compares the effects on the mud properties for EXP-154 with ALPLEX in 12 lb/gal 20% NaCl/NEW-DRILL/EXP-155 fluids. The experimental aluminum complex exhibits improved compatibility with latex and biopolymers. Additionally, EXP-154 is found to control filtration, both API and HTHP, better than does ALPLEX.

20

Pore Pressure Transmission Testing

[0060] Borehole stability effects of the experimental latex system were evaluated with the pore pressure transmission (PPT) tester previously described. A preserved Pierre II shale plug, 1 inch diameter by 0.9 inch long (2.54 cm x 2.29 cm 25 long), is placed between two pistons, as described previously in Example 2. The circumference of the shale and pistons sealed with a rubber sleeve. The plug is oriented with the bedding planes in the parallel or high permeability direction. Drilling fluid at 300 psi is displaced through the upstream piston (borehole side) and seawater at 50 psi is displaced through the downstream piston (formation side). 30 The seawater in the downstream piston is contained with a valve. As mud filtrate enters the borehole end of the plug, connate water in the shale is displaced into the

formation piston. This additional water compresses the water inside the piston causing the pressure to rise. The pressure increase in the formation piston water is measured as formation pressure (FP) rise.

[0061]   The EXP-154/EXP-155 fluid produces the best PPT results to date as shown in FIG. 5. The top curve is a standard salt/polymer. The next one down is ALPLEX, the next curve is an EXP-154/AIRFLEX 728 formulation, below that is the EXP-154/EXP-155 formulation, and finally at the bottom is a 80/20 ISOTEQ fluid, 25% CaCl2, 6 ppb CARBO-GEL, and 10 ppb OMNI-MUL. Without necessarily being limited to one explanation, the superior performance of the EXP-154/EXP-155 fluid is believed to be due, at least in part, to its small particle size. As discussed previously, GENCAL 7463 was more efficiently dispersed by the EXP-152 resulting in a much greater percentage of particles smaller than one micron.

[0062]   A synergistic effect between latex and aluminum complex has also been observed in these tests. Such results may be related to the co-precipitation behavior of EXP-155 and EXP-154. It was found that EXP-154 becomes insoluble at pH <10. At this condition, EXP-155 alone does not precipitate. However, when EXP-154 exists in this system, EXP-155 will be co-precipitated with EXP-154. Because of their co-precipitation behavior, deposited particles on the shale surface are comprised of lipophilic and hydrophilic components. This multiphase system is capable of creating a semi-permeable membrane, resulting in a great improvement in osmotic efficiency. Another characteristic of EXP-155 is that its ultra-fine particles are elastomer-like over a wide range of temperatures. When subjected to differential hydraulic pressure, these ultra-fine particles do not shear or break, but deform and penetrate the hairline fractures and to form an impermeable seal. At the temperatures between Tg (glass transition temperature) and Tm (melting point), most polymers will exhibit rubber-like elasticity. The glass transition temperature of EXP-155 is 52° F. From the relationship between Tg and Tm plotted by Boyer, 1963, reproduced in Billmeyer, Textbook of Polymer Science, Second Edition, Wiley-Interscience, New York, 1971, p. 230, we can estimate that Tm of EXP-155

is about 300°F (422°K). This temperature range covers most applications in drilling fluids.

[0063] Circulation of the fluid was found to be an important element of the latex plugging mechanism. This was explored in the tests with EXP-155. As the

5   formulation was only 1.5% latex particles by volume (EXP-155 is 50% active), insufficient latex was available in the mud to produce plugging under static conditions. With circulation, however, the latex accumulated on the surface and formed a plugging film. Standard procedure is to circulate the mud about 7 hours followed by static exposure overnight. Four or five hours without circulation elapses

10   before the test is started in the morning. This static period eliminates pressure drift due to temperature effects by allowing temperature variation from circulation to equilibrium.

[0064] When the test started the formation pressure fell from 50 psi to zero, increasing the differential pressure from 250 to 300 psi, as seen in FIG. 6. In about

15   30 hours, the plug began to leak and the formation pressure rose. However, additional circulation sealed the leak in an hour and the pressure again fell to zero. In previous tests the circulation was stopped after an hour, and the plug started leaking again after another 30 hours. In this test, circulation was restarted after the pressure rose to 60 psi in 70 hours (FIG. 6). However, circulation was maintained 5

20   hours instead of one as before. With a few hours of continued circulation after the greater pressure differential was established, the seal was more stable. The pressure rose only a few psi in 45 hours.

[0065] Photomicrographs of the plug face showed latex accumulation along microfractures in the shale. As the volume and velocity of filtration flow into these

25   cracks is very small, filtration alone cannot account for the latex accumulation at the crack throat. Inside these cracks the clay surface area to filtrate volume ratio is very large resulting in heavy EXP-154 precipitation. The reason may relate to the co-precipitation behavior of EXP-154 and EXP-155 as discussed previous, without being limited to any particular explanation. The precipitation of aluminum complex

30   at pH <19 apparently enhances latex accumulation at the crack throat. When

sufficient latex is deposited to bridge the crack opening, the fracture is sealed and differential pressure is established across the latex. The differential pressure consolidates the latex deposit into a solid seal. Increasing the differential pressure apparently causes this seal to deform over time (about 30 hours in the case of the

5 FIG. 6 results) and/or grows additional cracks in the shale and the shale begins to leak, although the inventors do not necessarily want to be limited by this explanation. However, additional circulation rapidly sealed the leaks and reestablished the seal. Circulating after the full differential pressure was reached formed a stable seal with only a small pressure rise.

10

Effect of Latex on Mud Properties

[0066] The previous results and discussions deal with latex stability in drilling fluids and its synergy with aluminum complex in improving mud inhabitability to shale formations. Besides, improved performance parameters achieved by the latex

15 products were also recognized. Two latex samples, Latex A (8:1 blended AIRFLEX 728 and EXP-152) and EXP-155 (8:1 blended GENCAL 7463 and EXP-152), were evaluated in 9.6 lb/gal 20% NaCl and 12 lb/gal 20% NaCl fluids. The effects of adding 3% by volume of these latex products are illustrated in FIGS. 7 and 8. Without obvious effect on the fluid rheology, HTHP fluid loss at 250°F (121°C)

20 decreased as much as 45% and 52% in 9.6 lb/gal mud and 35% and 40% in 12 lb/gal mud by Latex A and EXP-155, respectively. Again, EXP-155 presents better results that AIRFLEX 728. Additional tests with EXP-155 are listed in Table II.

TABLE II

Typical Performance Parameters of 12 lb/gal 20% NaCl/EXP-155 Fluids

Formulation Example #	23	24
Water, bbl	0.89	0.89
XAN-PLEX D, lb/bbl	0.5	0.5
BIO-PAQ, lb/bbl	4	-
BIO-LOSE, lb/bbl	-	4
NEW DRILL PLUS, lb/bbl	1	1
EXP-154, lb/bbl	5	5
NaCl, lb/bbl	77.5	77.5
EXP-155, % by vol.	3	3
MIL-BAR, lb/unweighted bbl	150	150
Rev-Dust, lb/bbl	27	27

Initial Properties		
PV, cP	22	21
YP, lb/100ft^2	26	20
10 second gel, lb/100ft^2	5	4
10 minute gel, lb/100ft^2	10	8
API, cm^3/30 min	2.5	1.4
pH	10.6	10.7
Density, lb/gal	12.2	12.2

	150°F (66°C)	250°F (121°C)	300°F (149°C)	150°F (66°C)	250°F (121°C)	300°F (149°C)
after HR 16 hr @	150°F (66°C)	250°F (121°C)	--	150°F (66°C)	250°F (121°C)	--
after static aged 16 hr @	--	--	300°F (149°C)	--	--	300°F (149°C)
PV, cP	20	21	22	26	24	23
YP, lb/100ft^2	24	29	34	17	21	22
10 second gel, lb/100ft^2	6	7	10	4	5	5
10 minute gel, lb/100ft^2	9	10	13	7	7	7
API, ml	2.8	3.7	2.8	2.2	2.6	1.8
pH	10.4	9.7	9.7	10.5	9.7	10.1
HTHP fluid loss, cm^3/30 min.	9.4	16.4	12	8.4	13	10.8

Toxicity Test

[0067]   The 96 hour range-finder bioassay results of AIRFLEX 728, GENCAL 7463, EXP-152, EXP-154 and EXP-155 in 12 lb/gal 20% NaCl/NEW-DRILL fluids are presented in FIG. 9. All products meet the requirement for fluid disposal in the Gulf of Mexico (30,000 ppm) and become less toxic after solids contamination.

Use of Polymer Latices in Oil-Based Fluids

[0068]   In another non-limiting embodiment of the invention, it has been discovered that polymer lattices within the scope of this invention, such as MAX-
5   SEAL, may be used as a sealing agent in oil base fluids when drilling depleted sand formation where mud loss might occur. This embodiment of the invention may also be used in at least partially sealing subterranean sand formations during other hydrocarbon recovery operations.

[0069]   FIG. 10 shows the particle size distribution of MAX-SEAL in ISO-TEQ
10   synthetic polyolefin drilling fluid. MAX-SEAL is dispersible in oil. Most particles of MAX-SEAL are in the range from 0.5 to 10 microns. The particles above 10 microns may come from the water in MAX-SEAL.

[0070]   The compatibility of MAX-SEAL with oil base mud has been tested in 14 lb/gal (1700 kg/m^3) SYN-TEQ mud. Table III gives the mud formulations with
15   and without MAX-SEAL. After aging at 250° F (121° C) for 16 hours, the mud sample with 3% MAX-SEAL was homogenous. The sealing ability of MAX-SEAL has been evaluated with a particle plugging apparatus (PPA) tests at 250° F (121° C) and 1000 psi (7,000 kPa) pressure differential using 0.4, 2 and 20 darcies cement disks respectively and the results are shown in FIG. 11.

20   [0071]   The sealing ability of MAX-SEAL increases with decrease in permeability. MAX-SEAL might be used with the best efficiency when drilling some low permeable depleted sand formation. Because of this deformable property, MAX-SEAL can seal very small pores and reduce the fluid losses of oil base mud in low permeable depleted sand formations where other lost circulation material (LCM)
25   might not work effectively. As shown by FIG. 12, without MAX-SEAL, the fluid loss rate through a 0.4 Darcies disk reached a constant after two hours. In contrast, the fluid loss rate of the mud with 3% MAX-SEAL continually decreased with time and finally reached to zero.

TABLE III
Formulations and Properti s of 14 lb/gal (1700 kg/m³)
SYN-TEQ with and without MAX-SEAL

	SYN-TEQ Base	Base + 3% MAX-SEAL
Formulation #	25	26
ISO-TEQ, bbl (m³)	0.57 (0.09)	0.57 (0.09)
CARBO-GEL, lb/bbl (g/l)	2 (5.7)	2 (5.7)
OMNI-MUL US, lb/bbl (g/l)	16 (45)	16 (45)
28% CaCl₂, bbl (m³)	0.1 (0.016)	0.1 (0.016)
MIL-BAR, lb/bbl (g/l)	327 (935)	327 (935)
CARBOTEC S, lb/bbl (g/l)	1 (3)	1 (3)
Rev Dust, lb/bbl (g/l)	27 (77)	27 (77)
MAX-SEAL, % by vol.	—	3
Initial Properties		
600 rpm @ 120° F (49° C)	62	81
300 rpm	35	47
200 rpm	25	36
100 rpm	16	24
6 rpm	5	9
3 rpm	4	7
PV, cP (Pa-s)	27 (0.027)	34 (0.034)
YP, lb/100 ft² (N/m)	8 (3.9)	13 (6.3)
10" Gel, lb/100 ft² (N/m)	6 (2.9)	10 (4.9)
10' Gel, lb/100 ft² (N/m)	7 (3.4)	12 (5.8)
Density, lb/gal (g/l)	14.4 (41.2)	14.2 (40.6)
Electric Stability	882	995
HTHP@250° F (121° C)on 0.4 Darcy Disk, ml/30 min	21	7
After HR @ 250° F (121° C) for 16 hours		
Note: After HR the sample with 3% MAX-SEAL was homogeneous and without any flocculation of MAX-SEAL.		
600 rpm @ 120° F (121° C)	77	96
300 rpm	45	59
200 rpm	35	45
100 rpm	23	30
6 rpm	9	11
3 rpm	7	9
PV, cP (Pa-s)	32 (0.032)	37 (0.037)
YP, lb/100 ft² (N/m)	13 (6.3)	22 (11)
10" Gel, lb/100 ft² (N/m)	11 (5.4)	13 (6.3)
10' Gel, lb/100 ft² (N/m)	13 (6.3)	17 (8.3)
Density, lb/gal (g/l)	14.4 (41.2)	14.2 (40.6)

Electric Stability	1073	895
PPA@250°F (121°C)on 0.4 Darcy Disk (3 μ), ml/30 min	(Spurt: 4 ml) 17 ml	(Spurt: 2 ml) 7 ml
PPA@250°F (121°C)on 2 Darcy Disk (10 μ), ml/30 min	(Spurt: 3.5 ml) 17.5 ml	(Spurt: 3.5 ml) 8.5 ml
PPA@250°F (121°C)on 20 Darcy Disk (60 μ), ml/30 min	(Spurt: 3.5 ml) 15.5 ml	(Spurt: 3.5 ml) 13 ml

[0072]   In the foregoing specification, the invention has been described with reference to specific embodiments thereof, and has been demonstrated as effective in providing a water-based or oil-based drilling fluid that can effectively reduce the

5   rate of drilling fluid pressure invasion of the borehole wall or partially or completely seal a subterranean sand formation. However, it will be evident that various modifications and changes can be made thereto without departing from the broader spirit or scope of the invention as set forth in the appended claims. Accordingly, the specification is to be regarded in an illustrative rather than a restrictive sense. For

10   example, specific combinations of brines or hydrocarbon base fluids and latexes and with optional emulsifiers, precipitating agents and/or wetting surfactants or salts falling within the claimed parameters, but not specifically identified or tried in a particular composition to reduce mud pressure penetration into shale or sand formations, are anticipated to be within the scope of this invention.

15

<div align="center">GLOSSARY</div>

4025-70	Low molecular weight amphoteric polymer sold by Amoco, found to be ineffective (also abbreviated as 4025).
20 AIRFLEX 728	A polyvinylacetate latex (more specifically, an ethylenevinyl chloride vinylacetate copolymer) dispersion sold by Air Products.
AIRFLEX 426	Vinyl acetate/ethylene copolymer available from Air Products.

	AIRFLEX 7200	Vinyl acetate/ethylene copolymer available from Air Products.
	ALPLEX®	Proprietary aluminum complex product available from Baker Hughes INTEQ.
5	AqS	Abbreviation for AQUACOL-S, a glycol available from Baker Hughes INTEQ.
	BIO-LOSE	Derivatized starch available from Baker Hughes INTEQ.
	BIOPAQ	Derivatized starch fluid loss additive available from Baker Hughes INTEQ.
10	CARBO-GEL	An amine-treated clay marketed by Baker Hughes INTEQ.
	CARBO-MUL	Invert emulsion emulsifier marketed by Baker Hughes INTEQ.
	CARBOTEC S	Emulsifier marketed by Baker Hughes INTEQ.
15	ELVACE 40722-00	Vinylacetate/ethylene copolymer latex available from Reichhold.
	EXP-152	Oleamidopropyl betaine surfactant.
	EXP-153	Sulfonated polymer resin (or sulfonated humic acid with resin) available from Baker Hughes INTEQ.
20	EXP-154	A mixture of 45% $NaAlO_2$, 45% EXP-153 and 10% sodium D-gluconate.
	EXP-155	An 8:1 volume blend of GENCAL 7463 and EXP-152.
	FLOWZAN	Biopolymer available from Drilling Specialties.
	FT-1 A	SULFATROL, 90% water-soluble sulfated asphalt
25		dispersion sold by Baker Hughes INTEQ.
	GENCAL 7463	Carboxylated styrene/butadiene available from Omnova Solution Inc.
	GENCAL 7470	Carboxylated styrene/butadiene available from Omnova Solution Inc.
30	GENFLO 576	Available from Omnova Solution Inc.

	ISOTEQ™	Synthetic, biodegradable, non-toxic, isomerized polyolefin-based drilling fluid available from Baker Hughes INTEQ.
5	LD8	A commercial defoamer available from Baker Hughes INTEQ.
	LIGCO	Lignite sold by Baker Hughes INTEQ.
	MAX-SEAL™	An aqueous suspension of sealing polymers available from INTEQ Drilling Fluids of Baker Hughes Incorporated.
10	MIL-BAR	Barite weighting agent available from Baker Hughes INTEQ.
	MIL-CARB	Calcium carbonate weighting agent available from Baker Hughes INTEQ.
15	MILPAC LV	Low viscosity polyamine cellulose available from Baker Hughes INTEQ (sometimes abbreviated as PacLV).
	NEWDRILL PLUS	Partially hydrolyzed polyacrylamide available from Baker Hughes INTEQ.
	OMNI-MUL™	A non-ionic emulsifier and wetting agent available from Baker Hughes INTEQ.
20	ROVENE 4823L	Styrene/butadiene copolymer available from Mallard Creek.
	ROVENE 6140	Carboxylated styrene/butadiene available from Mallard Creek.
25	ROVENE 9410	Carboxylated styrene/butadiene available from Mallard Creek.
	SA	Abbreviation for sodium aluminate.
	SYN-TEC^{SM}	Drilling fluid systems available from Baker Hughes INTEQ incorporating ISO-TEQ polyolefin-based drilling fluids along with other specialized fluid additives.
30	SYNTHEMUL 97982	Carboxylated acrylic copolymer available from Reichhold.

	SYNTHEMUL CPS 401	Carboxylated acrylic copolymer available from Reichhold.
	TYCHEM 68710	Carboxylated styrene/butadiene copolymer available from Reichhold.
5	TYLAC 68219	Carboxylated styrene/butadiene copolymer available from Reichhold.
	TYLAC CPS 812	Carboxylated styrene/butadiene copolymer available from Reichhold.
	VINAC XX-211	Vinyl acetate/ethylene copolymer available Air Products.
10	XAN-PLEX D	Biopolymer available from Baker Hughes INTEQ.